

## **Reply to the “Conceptual issue with the age of nitrate and number of recyclings” by Eric Wolff**

We warmly thank Prof. Eric Wolff for his additional feedback on this very key conceptual issue. His critical and constructive views on the calculation of the number of recyclings helped us to imagine a different approach.

Replies to Prof. Wolff’s remarks and suggestions are given below. For clarity, we keep the reviewer’s comments in blue and italic while our response is in black font.

### *Problems with calculation of archiving lifetime and number of recyclings*

Before addressing Prof. Wolff’s comments and suggestions, let us recall the purpose of introductory section 1.2 (ACPD version). The goal of this section was to demonstrate the choice of the concepts used in the TRANSITS model for the conditions prevailing at Dome C. Indeed, we need:

1. To demonstrate that the NO/NO<sub>2</sub> cycling is fast enough to consider that 100% of the O atoms in NO<sub>2</sub> originate from the local summer NO<sub>x</sub> chemistry, and,
2. To demonstrate that NO<sub>y</sub> (the sum of nitrate + NO<sub>x</sub>) are recycled many times at the air-snow interface before being archived.

Reconsidering the second point, it appears that there is not such a need to convince the reader that multiple recyclings occurs at the air-snow interface. Indeed, the part 1 paper has already provided a demonstration for the recycling of nitrate to take place at the DC air-snow interface, as also suggested initially by (Davis, et al., 2008). The question that remains is the number of recycling before nitrate is definitely archived. Because the processes involved in nitrate recycling (loss, oxidation and deposition) are represented in the model, the model should be able to quantify such number of recycling.

We also note that our definition of the number of recyclings was not clear. Indeed, while we referred to the number of recyclings undergone by nitrate at the air/snow interface, our approach was an attempt to calculate the number of recyclings that the archived nitrate underwent and not the recyclings of the nitrate pool within the photic zone. This conceptual difference is essential because the information which can be extracted from ice core are only those hold by the archived nitrate. In the following, we will clarify this point.

After rethinking the issue, it turns out that the calculation of the number of nitrate recyclings is far from evident. As a result, we suggest to remove the calculation of the number of nitrate recyclings from section 1.2 (p6892 L12-26, ACPD version) and to replace it by a discussion later in the text (e.g., in section 3.3). To support our choice, we are addressing Prof. Wolff’s comments and suggestions below.

*When I wrote my main review of this paper, I confessed to some conceptual uncertainty about the meaning of  $\tau_{arch}$ , and some surprise about the number of recyclings estimated by the authors (page 6892, para 2 and many subsequent parts of paper). I have now thought some more about this,, and have convinced myself there is a problem that the authors need to*

address. I hope that others who have considered this problem might come in, either to explain more formally what the correct calculation is, or to explain why I have got it completely wrong.

*Tau-arch* of course can be calculated, and ( $m_{50cm}/FA$ ) is certainly the time it would take to deplete the 50 cm box purely by archiving nitrate. However the authors assert that this is the lifetime of nitrate in the top 50 cm and therefore use this to estimate the number of photochemical recyclings each nitrate ion has undergone.

There must be a misunderstanding here. Indeed, we do not assert that *Tau-arch* is the lifetime of nitrate in the top 50 cm but that it is “the lifetime of nitrate in the top 50 cm against archival” (p6892, L20-21, ACPD version). Therefore, it seems that we agree on this definition:  $Tau\_arch = m_{50cm}/FA$ .

What struck me as odd about this calculation is that is blind to the magnitude of the primary input ( $FPI=FT+FS$ ), or  $f_{exp}$ . So let’s do some thought experiments in which the some of the values in Table 5 are varied, but still within physically allowed ranges. I have included the value of  $m_{50cm}$  and a calculated  $f_{exp}$ . All units are  $mg$  (or  $10^{-6} kg$ )  $N m^{-2}$ , or  $mg N m^{-2} a^{-1}$  as in the paper. Case A is the one in the paper. Cases B and C are the extreme ends of what is possible. In each case the amount in the top 50 cm and the amount archived ( $FA$ ) are kept the same as in the base case. But  $FPI$  is varied between the minimum that allows mass balance ( $FA$ ), and a very large number. I simply have to alter  $FE$  (and hence  $f_{exp}$ ) to balance the calculation.

	A (as in paper)	B	C
$m_{50cm}$	8.3	8.3	8.3
$FP$	32.00	32.00	32.00
$FD$	32.16	32.16	32.16
$FE$	8.04	999.84	0
$FA$	0.16	0.16	0.16
$FPI$	8.2	1000	0.16
$f_{exp}$	20%	Close to 100%	0%

Because of the fast photochemistry, the 50 cm firn box and the atmosphere are essentially a single box as far as mixing with the primary input is concerned. In case B there is a huge primary input. When nitrate in the firn is photolyzed, it is quickly swamped by new ( $FPI$ ) input, and whatever is deposited is almost entirely new input. In this case the lifetime of nitrate in the combined firn/atmosphere box (ignoring the physical transit time for an ion to be advected with the snow from the skin layer to below 50 cm) is close to zero, and all the ions that survive have likely never been recycled (zero recyclings).

Agreed.

In case C on the other hand, the primary input balances  $FA$  and the only way an ion can escape the combined box is by being archived. In this case the lifetime in the combined box is indeed 50 years, but that is calculated as  $FP/FPI$ , not as  $FP/FA$  as in the calculation of  $\tau_{arch}$  in the paper. The number of recyclings in this case is very high and may well be 120.

We agree that, in case C,  $\tau_{\text{arch}} = m_{50\text{cm}}/FA \approx 52$  years. We also note that the absence of an export on nitrate ( $FE = 0$ ) leads to the equivalence between the lifetime of nitrate against archival  $\tau_{\text{arch}}$  and the lifetime of  $\text{NO}_y$  in the combined atmosphere/snow box.

In correspondence with Prof. Wolff, he acknowledges that he wrote FP/FPI and FP/FA when he intended  $m_{\text{arch}}/FPI$  and  $m_{\text{arch}}/FA$ .”

*So, here is the point. The lifetime of nitrate (or perhaps I should say of  $\text{NO}_y$ ) in the combined 50cm/atmosphere box is NOT  $m_{50\text{cm}}/FA$ , but  $m_{50\text{cm}}/(FA+FE) = m_{50\text{cm}}/FPI$ , and this is what determines how old the nitrate in the box is and how many recyclings it has experienced. For the base case in the paper this is then of order 1 year and the average number of recyclings will be of order 10 I suppose.*

We thank Prof. Wolff for his demonstration that our assumption and the 120 cycles we report were incorrect. In the ACPD version, here is how we calculated the number of cycles:  $n_{\text{cycles}} = \tau_{\text{arch}} / \tau_{\text{photo}} = FP/FA$ . This choice was made by analogy with our calculation of the number of  $\text{NO}/\text{NO}_2$  cycles before  $\text{NO}_2$  is converted to  $\text{HNO}_3$  (section 1.2). It is now clear that this definition of  $n_{\text{cycles}}$  is not correct. Indeed, it seems unrealistic that this number can be as high as 120. While  $\text{NO}_y$  only remains in the combined 50cm/atmosphere box for one year on average, it is clear also that nitrate archived is older and as suggested by Prof. Wolff, 10 recyclings is probably more realistic.

In his demonstration, Prof. Wolff has to make a simple assumption by considering the photic zone as a single box and his calculation can only give an order of magnitude for the number of recyclings. In detail, this simple assumption ignores the heterogeneity of the photic zone box. The TRANSITS model is the perfect tool to make the correct calculation of the number of recyclings. Below, we suggest another approach to calculate  $n_{\text{cycles}}$  using the TRANSITS model.

*The critical point here is that the lifetime in a box is based on all the processes involved (Jacob 1999, eq 3.1). What we need to know the age of  $\text{NO}_y$  (the sum of nitrate +  $\text{NO}_x$ , for which we don't care about photolysis to  $\text{NO}_x$  except in so much as it mixes the 50 cm and atmosphere box) is, analogous to Jacob's eq 3.1*

$$\tau = m_{50\text{cm}}/(F_{\text{out}}+D) \quad (L \text{ is zero in this case as there is no chemical loss of } \text{NO}_y), \text{ ie}$$

$$\tau = m_{50\text{cm}}/(FE+FA).$$

*What the authors calculate as  $\tau_{\text{arch}}$  is  $m_{50\text{cm}}/FA$  which is the lifetime against archiving, but is not the one you need to estimate the age of the archived nitrate!*

We agree with Prof. Wolff as long as the photic zone is considered as a single box but this assumption is not true because the snow nitrate age is not homogeneous and 90% of the mass is within the first mm of the photic zone. This heterogeneity in age and concentration forbid the use of a two-box model. This is the reason why TRANSITS was built as a multi-layer model. Put in other words, FPI concerns only the “skin layer”, not the layers below. The lifetime

definition given by Prof. Wolff concerns essentially the lifetime of nitrate within the first top layer. Since this layer contains 90% of the mass, as a first approximation one can consider this lifetime as the lifetime of nitrate for the whole photic zone but in reality, this is not true. A good analogy is the atmosphere where the troposphere and stratosphere cannot be treated as a single box due to the large difference in lifetime within these two compartments. In the case of the photic zone, it is the same: the large heterogeneity between the top and the bottom precludes the use of a single box for the snow. For the DC atmospheric box, the BL is a well-mixed (at least at our time scale) and a single box approximation is valid. Only a multi-layer model can actually calculate the number of recycling as we will show below.

*Please tell me how I am wrong, but I think I am not! I am unsure why your model takes 20 years to equilibrate, but given that it takes around 15 years for surface snow to sink through the 1 meter snow model domain, it may simply be that. If I am right, the paper needs changing in several places including Fig 1, page 6938, 6936 and especially 6892, but the whole paper should be checked for errors based on this.*

### *Calculation of the average number of recyclings undergone by the archived nitrate using the TRANSITS model*

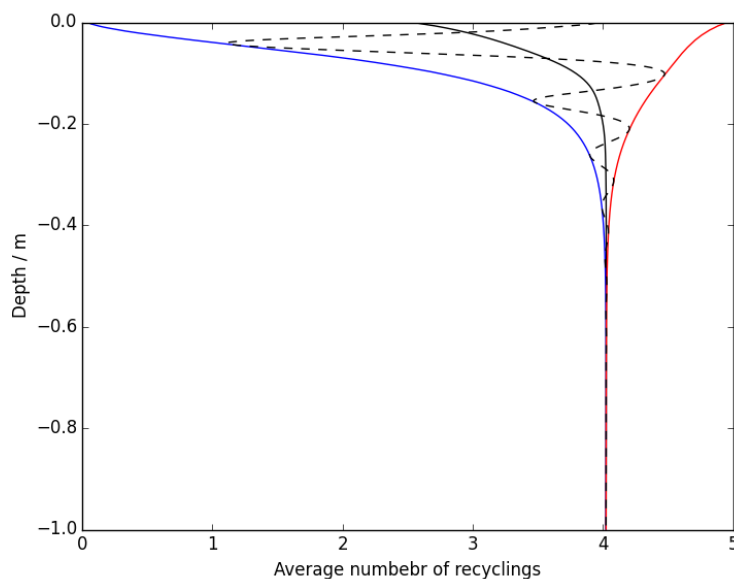
As clarified earlier in this document, we seek an information about the average number of recyclings undergone by the nitrate ions which are actually archived. We acknowledge that the range of number of recyclings undergone by the archive nitrate ions must be wide since some nitrate ions may well have travelled through the entire snowpack zone of active photochemistry without been recycled while some did undergo a lot of recyclings. We recall that one should not confuse “the average number of recyclings at the surface” and “the average number of recyclings of the archived nitrate ions”.

#### Method:

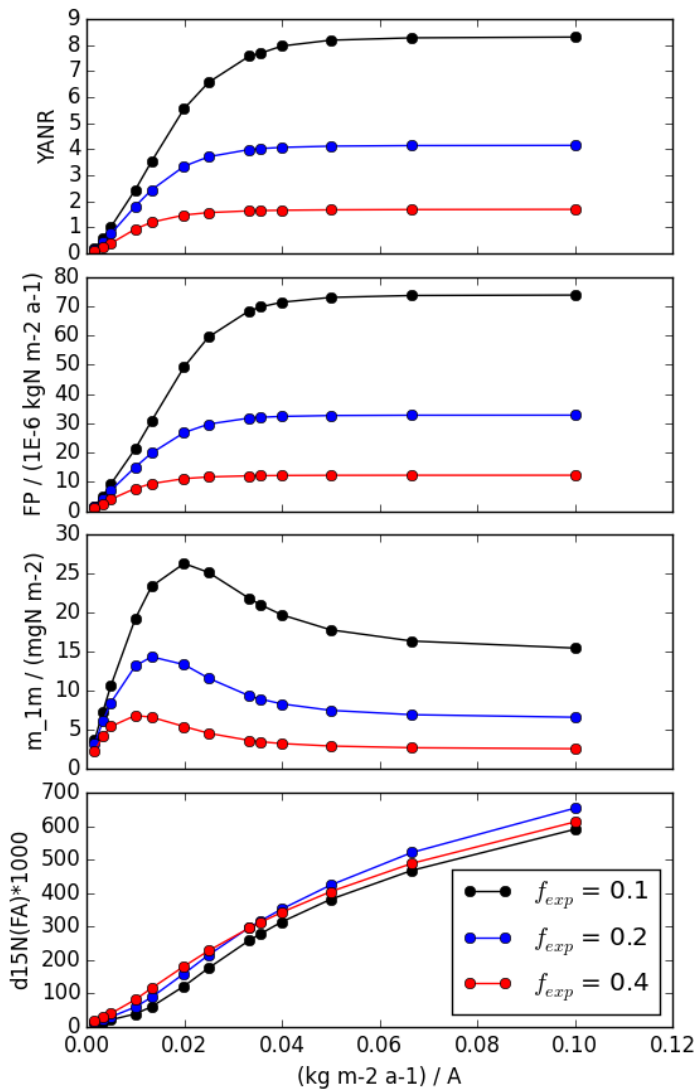
A new tracer, denoted “CYCL”, has been introduced in the TRANSITS model. In a given box (snow layer or atmosphere), *CYCL* represents the average number of recyclings undergone by nitrate in the considered box. The *CYCL* variable follows a numerical treatment which is comparable to that of  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ , i.e. a “recycling” (instead of an isotopic) mass balances, diffusion and the calculation of *CYCL* values in the macroscopic fluxes (*FP*, *FD*, *FE*, *FA*). The *CYCL* value for primary nitrate is set to 0 and *CYCL* variables in the boxes are incremented by 1 in the only case of the upward crossing of the air-snow interface by  $\text{NO}_2$  molecules (i.e. in the case of every photolytically produced  $\text{NO}_2$  molecules which do not undergo cage effect). Hereafter, *YANR* denotes the “Yearly Average Number of Recyclings” undergone by the archived nitrate. *YANR* is calculated as a mass-weighted average of the *CYCL* values of the 52 snow layers which are archived below 1 m over the course of one year. We have checked that *YANR* is insensitive to the chosen steps for time and space (snow) discretization (approx. one week and 1 mm for the DC realistic simulation, respectively).

For the Dome C simulation, we obtain  $YANR = 4.02$  which means that, on average, the archived nitrate at Dome C has undergone 4.02 recyclings (i.e. loss, local oxidation, deposition). The figure below shows the profile of ANR for summer solstice at Dome C.

The figure below shows the average number of recyclings as a function of depth in the DC realistic simulation. The black line represents the yearly average depth profile which shows that nitrate in the skin layer has undergone 2.6 recyclings on average and that CYCL values quickly increase in the top 20 cm where nitrate photolysis is the most active. The curves in blue and red indicate the yearly minimum and maximum of CYCL as a function of depth. This draws an envelope as observed in the case of the CYCL profile at summer solstice (black dashed line) which shows one-year period oscillations corresponding to the burial of the former “skin layers” which have high CYCL values. The dampening of the CYCL oscillations at depth is the result of nitrate diffusion in the snowpack.



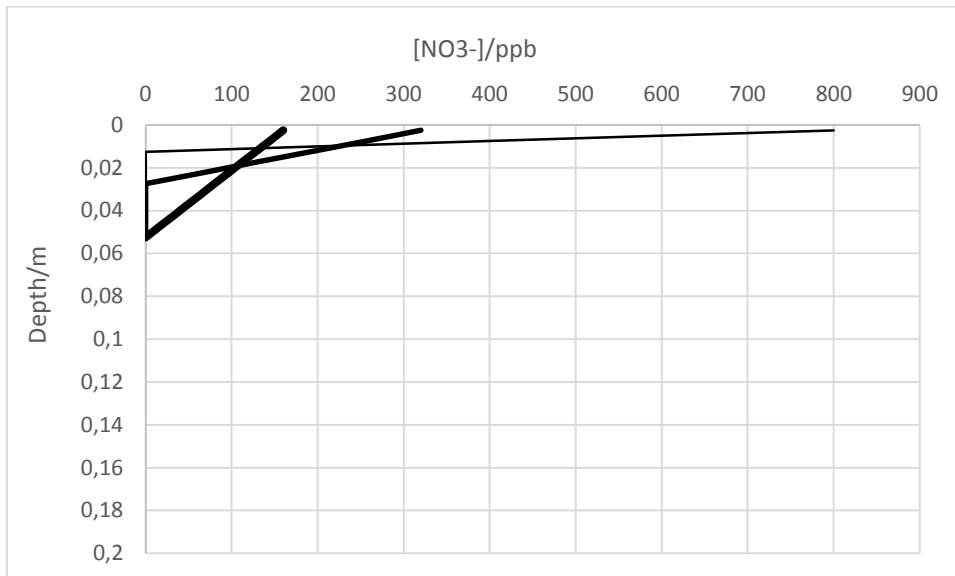
The figure below presents the results of an experiment where the annual snow accumulation rate ( $A$ ) and the export parameter ( $f_{exp}$ ) have been varied. We report  $YANR$ ,  $FP$ ,  $m_{1m}$  (the nitrate mass in the top 1m of the snowpack) and  $d_{15N}(FA)$  in the archived nitrate as a function of the inverse of the snow accumulation rate ( $1/A$ ).



At a given  $f_{exp}$  value and for  $A > 50 \text{ kg m}^{-2} \text{ a}^{-1}$  ( $1/A < 0.02$ ), YANR first linearly increases with the increase in  $1/A$  which means that the burial of snow layers controls nitrate recycling. For low snow accumulation rates ( $A < 20 \text{ kg m}^{-2} \text{ a}^{-1}$ , i.e.  $1/A > 0.05$ ), YANR reaches a plateau at 4.1 in the case where  $f_{exp} = 0.2$  (DC case). The second panel on the above figure shows that YANR and FP have concurring variations. We recall that  $\text{FPI}$  is kept constant at  $8.2 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$  in these experiments and observe that  $\text{YANR} = \text{FP}/\text{FPI}$ . In this second regime, the burial of snow is no longer limiting and the snowpack control on YANR ceases because nitrate is confined in the top layers (discussed below).

For low snow accumulation rates ( $A < 20 \text{ kg m}^{-2} \text{ a}^{-1}$ , i.e.  $1/A > 0.05$ ), we also observe that FP remains constant, e.g. at  $32.8 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$  for  $f_{exp} = 0.2$ . The reason is that, while the residence time of nitrate in the photic zone increases with the decrease of  $A$  (mass loss increases for a fixed time step), the nitrate concentration profile at depth diminishes (the mass loss decreases for the same time step), so that at the end, FP levels off due to the negative

feedback of the decreasing nitrate concentration. In this extreme case,  $m_{1m}$  does not change significantly (third panel on the figure above). The schematic figure below shows how nitrate distributes with depth with the decrease of  $A$ . The decrease in line thickness represents the decrease in snow accumulation rates ( $A$ ). When  $A$  decreases, most of nitrate gets confined in a layer at the top which becomes thinner.



Our finding of  $YANR = FP/FPI$  is an independent confirmation of the definition given by Davis et al (2008) on the basis of the macroscopic yearly primary and photolytic fluxes: the “Nitrogen Recycling Factor”,  $NRF = \text{ratio of nitrogen emission and nitrogen deposition}$ . While we are satisfied to end up with the Davis et al (2008) expression for  $YANR$  using our independent model-based tracer experiment, we must observe that we define  $YANR$  is the average number of recyclings undergone by the archived nitrate while Davis et al (2008) define it as the “nitrogen recycling factor within a photochemical season”.

In our experiments above, we have observed that a key control on  $FP$  and, thus,  $YANR$  is  $f_{exp}$  which sets the degree of horizontal export of nitrate in the atmosphere. All else being equal, increasing values of  $f_{exp}$  lead to the increase of the exported flux ( $FE$ ), to the lower incorporation of atmospheric nitrate to the snow and, in turn, to lower  $FP$  values.

### Conclusions:

From this small study, it seems that the average number of recyclings undergone by the archived nitrate at Dome C is around 4.02. This value seems more reasonable than the value 120 we have calculated previously. We recall that our definition of  $YANR$  was wrong in the ACPD version of the paper and led to this false value. If Prof. Wolff agrees with our approach to calculate  $YANR$ , we suggest:

1. to remove the reference in the calculation of the number of recyclings in the introduction (second paragraph of section 1.2)
2. to remove the mention of a number of cycles of 120 (and of course 150) in the text
3. to update figures 1 and 11

4. to incorporate the results and discussion of the above small study in section 3.3 where we discuss the model results.

### *Note on the time for the model to reach equilibrium*

In the paper we state that the model takes 20 years to equilibrate. Given that it takes approximately 10 years for a surface layer to get buried below 1m depth in conditions close to DC conditions ( $A = 30 \text{ kg m}^{-2} \text{ a}^{-1}$  and  $\rho = 300 \text{ kg m}^{-3}$ ), why are those two numbers different?

In order to get an objective view on the time to equilibrium (hereafter denoted "TTE"), we simulate a "spike" of nitrate in the atmospheric box. In the middle of summer, a nitrate mass equivalent to one year of nitrate input (FPI) is deposited to the top layer. We could label this nitrate with a very special isotope signature but we can also simply monitor the time the archived nitrate mass takes to reach equilibrium after the "spike nitrate" has escaped below 1m.

The sudden nitrate mass which adds up to the atmospheric box is simulated as follows:

- mass =  $8.2 \cdot 10^{-6} \text{ kgN m}^{-2}$  (same as one year in a week)
- Sudden mass gain happens after 20 years of computation when the model has reached stability and at summer solstice (time step 26)

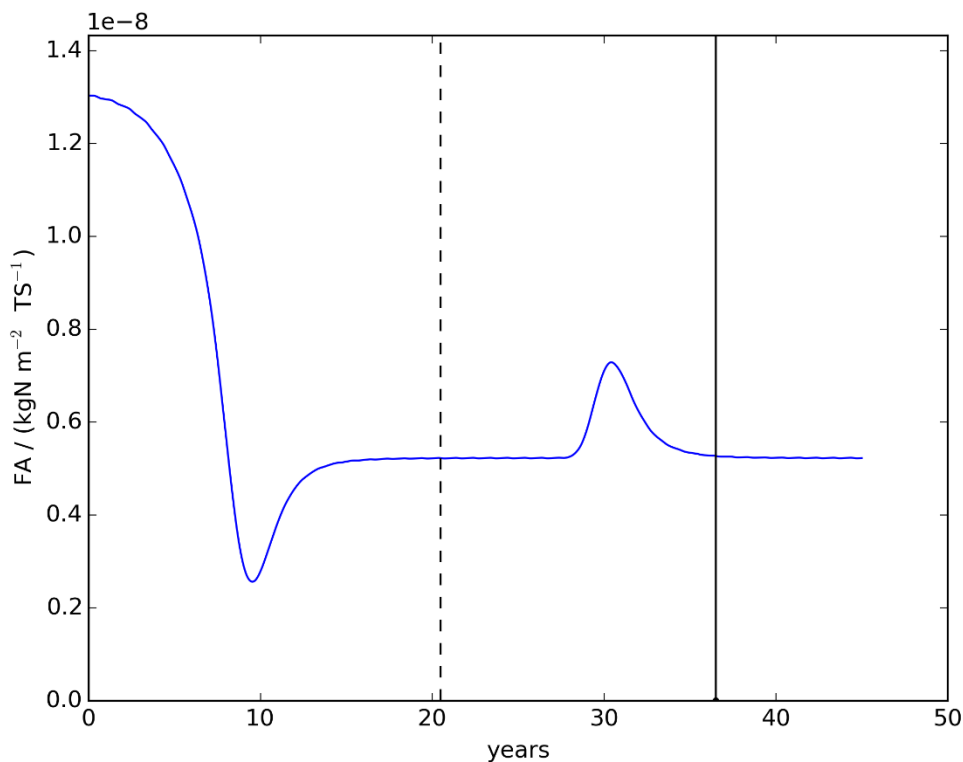
The model is used in DC conditions:

- $\Phi = 0.026$
- $\text{Diff} = 1.33 \cdot 10^{-11} \text{ cm}^2 \text{ s}^{-1}$
- To simplify, we use  $A = 30 \text{ kg m}^{-2} \text{ a}^{-1}$
- $\rho = 300 \text{ kg m}^{-3}$

The residence time of nitrate in the top 1m of the modeled snowpack is the average time for the nitrate ions from the spike to get below 1m. However, when it comes to looking at equilibrium, we look for the time it takes to – ideally – archive 100% of the nitrate ions from the spike. To calculate this duration, we observe the time when the archived mass (FA) is getting back to its "equilibrium value" within 1%.

Below is an example with the DC case described above (Case 1 in table below). The y-axis represents the nitrate mass which is archived below 1m at every time step. The x-axis represents the time (in years) after the beginning of the computation. The first phase (0-20 years) shows the equilibration of the model. The vertical dashed line represents the time when the sudden nitrate mass adds up in the atmosphere (i.e. after  $20 + 26/52 = 20.5$  years). The vertical line to the right represents the time when FA gets back within +/- 1% of the "equilibrium value" (i.e. approx.  $5 \cdot 10^{-9} \text{ kgN m}^{-2} \text{ TS}^{-1}$ ). In this case, the "spike nitrate" took 16 years to fully escape the photic zone. We also observe that the very first ions originating from this "spike nitrate" archive 8 years only after deposition, which means, faster than the snow (10 years). This results from the nitrate diffusion in the snowpack.





We have investigate 2 other cases as depicted in the table below.

	Local recycling	Diffusion	Photolysis	TTE / years
1	Yes, $f_{exp} = 0.2$	$1.33 \cdot 10^{-11}$	0.026	16
2	Yes, $f_{exp} = 0.2$	No	No	11
3	Yes, $f_{exp} = 0.2$	No	0.026	16

Case 1 represents the conditions for the run displayed in the above figure. Case 2 represents the case where there is no photolysis and no diffusion. In this case, nitrate archives at the same rate as snow does and the TTE value (11 years) compares well with the residence time which is calculated ( $1m / (A / \rho) = 10$  years). Note, that the TTE value is an approximation which is overestimated given the way we calculate it.

The comparison of cases 1 and 2 shows that the photolytic and diffusion processes lead to a TTE which is increased by 5 years. In case 3, the diffusion process is switched off and we observe that the TTE is not changed. This shows that the N recycling initiated by nitrate photolysis is mostly responsible for the observed 5-year delay. In other words, the 6.4 recyclings undergone by the archived nitrate induces a 5-years delay in its burial.

Our observation in case 1 explains why the model takes almost 20 years to equilibrate. Note that the 20-year value reported in the ACPD version of the paper was an approximate value.

At last, we note that the experiment presented here could be helpful to discuss the potential archive of the nitrate production effects of Solar Proton Events (SPE) in Antarctic plateau firn and ice (see discussion in (Wolff, Jones, Bauguitte, & Salmon, 2008)). The small study above

for example shows that a fraction of the nitrate mass brought by a SPE could potentially be archived. Measuring  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  profiles in this archived nitrate could potentially help assessing whether or not an archived spike originates from a SPE. Of course, this is out of the scope of the present paper.

## References

- Davis, D. D., Seelig, J., Huey, G., Crawford, J., Chen, G., Wang, Y., . . . Eisele, F. (2008). A reassessment of Antarctic plateau reactive nitrogen based on 2003 airborne and ground based measurements. *Atmos. Environ.*, *42*, 2831-2848.
- Wolff, E. W., Jones, A. E., Bauguitte, S. J.-B., & Salmon, R. A. (2008). The interpretation of spikes and trends in concentration of nitrate in polar ice cores, based on evidence from snow and atmospheric measurements. *Atmos. Chem. Phys.*, *8*, 5627-5634.